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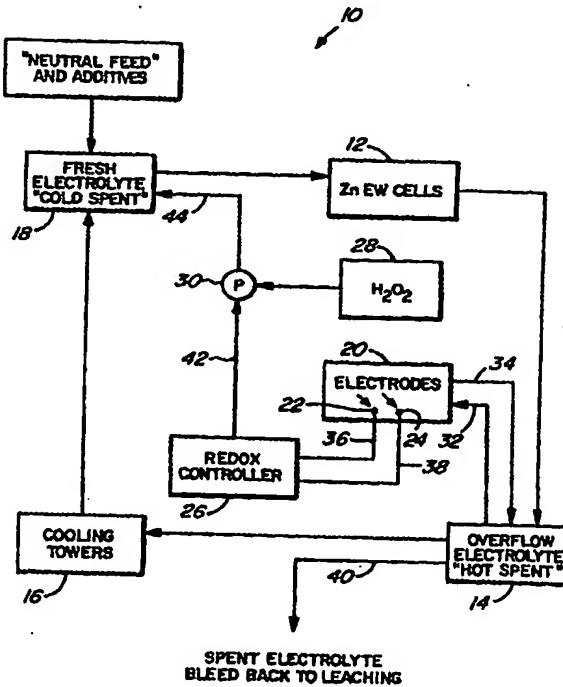
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(54) Title: REDOX CONTROL IN THE ELECTRODEPOSITION OF METALS

(57) Abstract

In one embodiment, a method of electrowinning a metal from an electrolyte comprises the steps of measuring the redox potential of the electrolyte to obtain a measured value, comparing the measured value with a predetermined optimum value and adding a redox agent to the electrolyte to adjust the redox potential of the electrolyte to the optimum value. One embodiment of apparatus (10) for carrying out the method comprises a redox potential measuring device (20) having a housing for the flow of electrolyte therethrough and including a pair of electrodes (22, 24) for measuring the redox potential of an electrolyte flowing through the housing to produce an output measurement value and a redox controller (26) responsive to the output measurement value for controlling the addition of redox agent to the electrolyte of an electrolysis cell (12).



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REDOX CONTROL IN THE ELECTRODEPOSITION OF METALSFIELD OF THE INVENTION

5 This invention relates to the electrodeposition of a metal from an electrolyte. In particular, but not exclusively, the invention relates to the electrowinning of a metal, such as zinc from zinc sulphate solution, as well as the on line or off line cleaning of an 10 electrolysis cell or an electrode of the cell.

BACKGROUND OF THE INVENTION

15 In the electrolysis of metals various ionic species can become oxidized or reduced. Thus, unwanted chemical products can be produced. Some of these products precipitate and need to be removed mechanically. Furthermore, such unwanted oxidation-reduction processes can consume electrons that could otherwise be used for 20 the plating of metals, thus, reducing the efficiency of the electrowinning process.

25 Typically, in the zinc electrowinning industry the Faradaic cathodic current efficiency (CE), i.e. the portion of the current which is actually utilized for the plating of the zinc, ranges from about 88% to about 93%. The difference between this CE value and the 100% value is due to the unwanted evolution of hydrogen and the presence of unwanted redox couples that consume 30 electrons, such as $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}$.

35 Another factor that affects the CE value is the anode quality and its electrochemical properties. In the electrowinning of zinc, Pb-Ag anodes are normally used. These anodes develop a PbO_2 layer upon which O_2 evolution and other side reactions can take place. Among the most

important of these is the formation of MnO_2 . MnO_2 precipitates on the anode increasing the so-called anodic overpotential and it also precipitates in the cell. This requires frequent anode cleaning which involves the

5 removal of the anodes and the mechanical cleaning thereof. The precipitates that accumulate at the bottom of the cell also need to be removed periodically. These operations often require a plant shutdown, unless expensive mechanized vacuum units are used.

10

It is an object of the present invention to alleviate the above-mentioned difficulties.

SUMMARY OF THE INVENTION

15

According to the invention there is provided an electrolysis process wherein an electric current is passed through an electrolyte to effect a chemical change, which includes the step of maintaining the redox 20 potential of the electrolyte within a predetermined range of values by adding a redox agent to the electrolyte.

The process may further comprise the steps of continuously monitoring the redox potential of the 25 electrolyte and adding said redox agent to maintain the redox potential of the electrolyte within said predetermined range of values.

The electrolysis process may comprise an 30 electrowinning process, an electrorefining process or an electroplating process.

Also according to the invention there is provided a method of electrowinning a metal from an 35 electrolyte comprising the step of maintaining the redox

potential of the electrolyte within a predetermined range of values by adding a redox agent to the electrolyte.

5 Further according to the invention there is provided a method of electrowinning a metal from an electrolyte comprising the steps of measuring the redox potential of the electrolyte to obtain a measured value; comparing said measured value with a predetermined optimum value; and adding a redox agent to the
10 electrolyte to adjust the redox potential of the electrolyte to said optimum value.

The term "redox agent" refers to either an oxidizing agent or a reducing agent.

15 Further according to the invention there is provided apparatus for controlling the redox potential of an electrolyte, comprising a redox potential measuring device for measuring the redox potential of an
20 electrolyte to produce an output measurement value; and a redox controller responsive to said output measurement value for controlling the addition of redox agent to the electrolyte of an electrolysis cell.

25 Also according to the invention there is provided a method of reducing the formation of an electrolysis product on an electrode of an electrolysis cell comprising the step of performing an electrolysis process in the cell with an electrolyte in which a redox agent is added which counteracts the formation of said product.

30 Further according to the invention there is provided a method of cleaning an electrolysis cell of an electrolysis product formed in the cell, comprising the step of performing an electrolysis process in the cell

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with an electrolyte to which a redox agent is added which counteracts the formation of said product.

Further according to the invention there is
5 provided a method of reducing MnO₂ formation in an electrolysis cell in a zinc electrowinning process, comprising the steps of measuring the redox potential of the electrolyte to obtain a measured value; comparing the measured value with a predetermined optimum value; and
10 adding a redox agent to the electrolyte to adjust the redox potential of the electrolyte to the optimum value.

Also according to the invention there is provided a method of reducing current efficiency loss in
15 an electrolysis cell in a zinc electrowinning process, comprising the steps of measuring the redox potential of the electrolyte to obtain a measured value; comparing the measured value with a predetermined optimum value; and adding a redox agent to the electrolyte to adjust the
20 redox potential of the electrolyte to the optimum value.

Further objects and advantages of the invention will become apparent from the description of a preferred embodiment of the invention below.

25

BRIEF DESCRIPTION OF THE DRAWINGS

The single drawing is a flow diagram illustrating an electrowinning and redox control process
30 according to the invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

With reference to the drawing, a system for
35 carrying out a process for the electrowinning of zinc

according to the invention is generally indicated by reference numeral 10.

5 The system 10 comprises a series of electrolytic cells 12, a reservoir 14 for overflow electrolyte ("hot spent") electrolyte from the cells 12, a series of cooling towers 16 for cooling the hot electrolyte from the reservoir 14 and a reservoir 18 for fresh electrolyte, as well as cold spent electrolyte from 10 the cooling towers 16.

15 The system 10 further includes a redox potential measuring device 20 provided with a working electrode 22 and a reference electrode 24, a redox controller 26 and a reservoir 28 for H_2O_2 . The reservoir 28 is connected to the reservoir 18 via a pump 30 which is controlled by the redox controller 26 responsive to redox potential measurements effected by the measuring device 20.

20 The working electrode 22 is a platinum or a silver electrode. The reference electrode 24 is a commercially available calomel or silver/silver chloride electrode.

25 The control of the redox potential can be effectively achieved only when the proper sensing electrodes are used. Platinum is very sensitive to small changes in the redox potential and abrupt changes in 30 value can be observed when this electrode is used. However, with the proper process control design, good redox control (within 50 mV) can be achieved. Graphite electrodes have a slower response than platinum and because of this do not display erratic readings. Thus, 35 when graphite is used, changes in redox potential are not as abrupt as those observed with platinum. Thus, a

preferred working electrode has been found to be graphite. In laboratory size electrowinning cells, when a graphite electrode is used, redox control can be achieved to within 20 mV.

5

The redox controller 26 comprises the required electronic circuitry and software for receiving and interpreting a signal representing the measured value from the measuring device 20 and to control the delivery of the required amounts of H_2O_2 to the reservoir responsive to the redox measurements by the measuring device 20.

15

The measuring device 20 is provided with a flow channel (not shown) for the flow of a feed stream of electrolyte therethrough. The electrodes 22 and 24 are exposed to the electrolyte flowing through the channel for measuring the redox potential of the feed stream. As indicated by the arrows 32 and 34, the electrolyte feed stream is circulated from the reservoir 14 containing the overflow (hot spent) electrolyte, which is essentially equivalent to the electrolyte in the cells 12.

25

The electrodes 22, 24 are connected through electrical connections 36 and 38 to the electronic circuitry of the redox controller 26.

30

In carrying out a zinc electrowinning process, the pregnant aqueous zinc solution plus the usual additives, which constitutes the "fresh electrolyte", is fed to the reservoir 18 where it is mixed with cold spent electrolyte from the cooling towers 16.

35

From the reservoir 18 the electrolyte is transferred to the electrolytic cells 12 where the electrodeposition of zinc takes place.

Spent electrolyte overflow from the cells 12 is received by the reservoir 14, from where the electrolyte is circulated through the redox measuring device 20.

5 There is a bleed of spent electrolyte from the reservoir 14, as indicated by the arrow 40, which in the conventional process for the recovery of zinc from ore or concentrate is recycled back to a leaching stage, where zinc is leached from the ore or concentrate by a suitable leach solution.

10

A part of the hot spent electrolyte in the reservoir 14 is transferred to the cooling towers 16 for cooling and recycle to the fresh electrolyte reservoir 18.

15

20 The redox controller 26 is in electrical contact, as indicated at 42, with the pump 30 for controlling the operation of the pump 30. The pump 30 pumps H_2O , from the reservoir 28 to the fresh electrolyte reservoir 18, as indicated by the arrow 44. It is desirable that the reducing agent being added be well mixed with the electrolyte prior to its addition to the electrowinning cells 12.

25

30 In operation, when the measured value of the redox potential from the measuring device 20 falls outside a predetermined optimum range, the redox controller 26 will activate the pump 30 to inject the required amount of H_2O , into the tank 18 to bring the measured value within the optimum range. The optimum range will depend on the particular system involved.

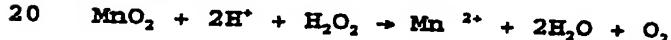
35 In particular, the optimum range is determined by aspects such as anodic and cathodic current density, the age of the anode, the composition and temperature of the electrolyte and the concentration of additives in the

electrolyte. The optimum range for each particular system therefore needs to be determined empirically.

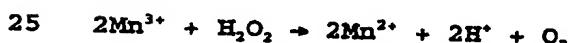
Therefore, to implement this technology in the industrial environment, laboratory and plant tests need to be conducted in advance to identify the optimum redox potential values at which the electrowinning process needs to be run. In the preferred practice for one zinc electrowinning operation, the optimum redox value was found to be 1040±50 mV (Pt vs H₂/H⁺ electrode).

The H₂O₂ can be added in diluted or concentrated form, preferably in concentrations higher than 35% so that no significant amounts of water are added to the system.

The reaction between H₂O₂ and MnO₂ occurs without kinetic limitations according to the following equation:



In addition, the following reaction can take place upon H₂O₂ addition:



Thus, by using a suitable reducing agent, such as H₂O₂ in the present example, unwanted chemical products such as MnO₂, Mn³⁺ and Mn²⁺ can be continuously removed.

30 The extent to which these reactions take place is controlled by control of the redox potential of the electrolyte. The invention therefore provides a process for the on line or off line cleaning of the cell and anode which increases plant availability and reduces the need for mechanical anode and cell cleaning. In addition, anode life is increased due to a decreased

frequency of short circuits caused by excessive or uneven anode coatings.

Instead of direct measurement of the redox potential an indirect measurement can also be used. For example, in situations where there is a correlation between redox potential and solution color, such as in zinc electrowinning from sulphate media, a colorimeter can be used for controlling redox potential, although direct E_h measurement would be more precise.

In laboratory tests which were carried out the electrolyte cells were run in series under galvanostatic conditions. Electrolyte temperature was controlled at 37±1°C. Electrolyte was recirculated to rates equivalent to the displacement of 1 to 1.5 cell volumes per hour. The E_h of the electrolyte was measured using calibrated bright Pt - calomel electrode pairs. E_h values reported are referred to the H_2/H^+ electrode. The E_h was controlled by adding diluted H_2O_2 (~3%) to the recirculating electrolyte. The E_h electrodes were placed in the cell overflow.

The initial electrolyte was prepared from purified zinc electrolyte and reagent grade sulphuric acid. The concentrations of Zn and H_2SO_4 were maintained constant by neutral feed additions and continuous electrolyte removal via the overflow weir. Electrolyte composition ranged between 61 and 64g/L of Zn and 148 and 155 g/L of H_2SO_4 . The neutral feed Mn concentration was 2.0 g/L. Glue concentration was 2.5 mg/L.

Two central Pg-Ag anodes and four opposing H1S Aluminum cathodes were used. The end cathodes were masked on their back and edges with epoxy resin. The immersed anode dimensions were 6.5 cm x 12 cm. The

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immersed cathode dimensions were 9.3 cm x 10.8 cm (central cathodes) and 8.2 cm 11.5 cm (end cathodes). Electrolyte cell volume was 7.3 L. The cathodic current density was set at 440 A/m².

5

Anodic and cathodic overpotentials were measured at preset intervals using a saturated Ag/AgCl reference electrode mounted in a Luggin capillary.

10

Eight continuous tests (Examples 1 to 8 in Table 1) were conducted using "freshly preconditioned anodes" and three cells connected in series. Each of these tests lasted from 43 to 74 hours. Fresh synthetic electrolyte was only used at the beginning of the test (in Example 1). Subsequent tests used the final electrolyte from the previous test.

20

Anodes were preconditioned in a KF-H₂SO₄ electrolyte (34 g/L F, 19 g/L of H₂SO₄) at 40° C at an ACD of 420 A/m² for 24h.

25

The E_h of these cells was controlled as follows:
Cell 1 No E_h control ("Natural E_h conditions")
Cell 2 E_h controlled at 1040 mV
Cell 3 E_h controlled at 1140 mV (occasionally E_h was controlled at lower values)

30

The mud deposited in the bottom and walls of the cell and on the cathode edgesticks was manually removed (with H₂O₂) after the end of Examples 1 (1st Exchange cycle), 3 (3rd Exchange cycle) and 8 (8th Exchange cycle). This was necessary to perform a mass balance on Mn and Pb deportment.

Table 1 Summary of Results Obtained in Continuous Experiments 1 to 8

Examples	EW Cycle hours	Cell No. 1		Cell No. 2		Cell No. 3				
		CE, %	[Pb] in Zn, ppm	[Mn] drop, g/L	CE, %	[Pb] in Zn, ppm	[Mn] drop, g/L	CE, %	[Pb] in Zn, ppm	[Mn] drop, g/L
1	68.9	87.3	100	0.50	93.4	46	0.60	87.0	39	0.25
2	42.8	92.0	28	0.40	93.4	41	0.35	92.1	26	0.25
3	43.3	92.5	17	0.90	93.9	17	0.85	90.5	18	0.60
4	42.9	77.7	64	0.90	92.2	33	0.70	89.5	30	0.55
5	45.4	90.3	16	0.85	94.5	22	0.50	89.5	6	0.50
6	73.5	90.0	13	0.15	94.9	6	0.00	89.1	5	0.00
7	49.7	91.8	7	0.40	94.9	4	0.30	92.3	6	0.30
8	47.6	91.2	7	0.40	94.9	4	0.36	92.4	6	0.36
Average	51.8	89.2	31	0.56	94.1	22	0.46	90.1	17	0.35

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As an indication of the precipitation of insoluble Mn precipitates, the difference in soluble manganese concentration and the average [Mn] in the electrolyte was used:

$$[Mn]_{drop} = [Mn]_{neutral\ feed} - \frac{[Mn]_{initial\ electrolyte} + [Mn]_{final\ electrolyte}}{2}$$

5

The larger the $[Mn]_{drop}$, the larger the amount of MnO_2 that precipitated in each cell.

Changes in CE, lead deportment to cathode Zn, 10 and $[Mn]_{drop}$ as a function of electrolysis time are shown in Table 1. The continuous run lasted 414 h. E_h control was possible within 50 mV of the set point although excursions as high as 200 mV away from it were often observed. This is attributed to the use of Pt sensing 15 electrodes which are very sensitive to small variations in the concentration of redox species in the electrolyte.

The highest CE values were obtained when the E_h 20 was controlled at about 1040 mV (cell 2). On an average, the CE obtained in cell 2 was 94.1% whereas the CE in cell 1 (a cell without E_h control) averaged only 89.2%. Average CE in cell 3 was 90.1%. E_h values in cell 1 were between 1350 and 1500 mV. In the last four EW cycles 25 (Examples 6 to 8) the CE in cell 2 was very high (94.5% to 94.9%) and reproducible.

While short circuits developed in cell 1 in the first and fourth electrodeposition cycles, no short 30 circuits were detected in cells 2 and 3 in any of the electrodeposition cycles. Deposits obtained with E_h control were polycrystalline and smooth, except in the first cycle in which pitting was observed in all the deposits. In all the experiments, Zn deposits could be

stripped just as easily as those obtained without E_h control.

As shown in Table 1, [Pb] in cathode Zn decreases with electrolysis time. The cells in which the E_h was controlled gave the lowest Pb deportment. On an average, the lowest Pb deportment was obtained in cell 3, followed (in increasing order) by those obtained in cells 2 and 1. It is important to stress that this low Pb deportment was obtained without SrCO₃ additions to any of the cells. Usage of H₂O₂ did not enhance the corrosion rate of the anodes or the Pb content of the cathodic zinc.

From Mn mass balances it was found that the percentage of Mn losses (e.g., "insoluble" manganese leftover in the cell walls and on the anodes) in cells 2 and 3 (25.9% and 20.6%) was smaller than those obtained in cell 1 (28.4%). Furthermore, the total amount of mud formed in the cells with E_h control (6.1 g in cell 2 and 4.1 g in cell 3) was significantly lower than in the cell without E_h control (9.5 g). As shown in Table 1, the [Mn] _{drop} observed in cells 2 and 3 was lower than in cell 1. This provides further evidence that the H₂O₂ treatment is very effective towards MnO₂ solubilization. Although lower [Mn] drops were observed in cells 2 and 3 this did not reflect in increases in Pb deportment, suggesting that H₂O₂ usage could extend the life of the anodes. As the anodes release less Pb into the cathodic Zn, the H₂O₂ consumption decreases, so that at the end of the continuous electrolyte cycle H₂O₂ consumption was as low as 1 Kg H₂O₂ (100%) per ton of Zn. The tests conducted so far, suggests that, on an average basis, 2 Kg of H₂O₂ (100%) per ton of Zn could be required to maximize the CE.

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decomposition (H_2O and O_2) are compatible with the Zn EW process. Furthermore, the high selectivity of H_2O , to reduce Mn^{3+} and MnO_2 , to Mn^{2+} without destroying the PbO_2 layer or the aluminum cathodes (H_2O , can be stored in 5 aluminum containers) made the use of H_2O , very competitive.

As found in several laboratory experiments, the 10 largest increases in CE with redox control are seen with "new anodes". If MnO_2 formation is reduced, short circuits could be prevented causing an increase in anode life and a decrease in the deportment of lead to the cathodic Zn deposit.

15 The process above has been described with reference to the electrowinning of a metal from an electrolyte, but it is contemplated that the process can also be applied to electrorefining and electroplating operations.

20 While only preferred embodiments of the invention have been described herein in detail, the invention is not limited thereby and modifications can be made within the scope of the attached claims.

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WHAT IS CLAIMED IS:

1. A method of counteracting the formation of MnO₂ precipitate in a process for the electrowinning of a metal from an electrolyte, which comprises the steps of:
 - 5 measuring the redox potential of the electrolyte to obtain a measured value,
 - 10 comparing the measured value with a predetermined optimum value; and
 - 15 adding a redox agent to the electrolyte to adjust the redox potential of the electrolyte to the optimum value.
- 15 2. The method according to claim 1, wherein the metal is zinc and the redox agent is hydrogen peroxide.
- 20 3. The method according to claim 1 or 2, wherein the measuring of the redox potential of the electrolyte comprises measuring the redox potential of a feed stream of electrolyte substantially equivalent to the electrolyte present in an electrolysis cell in which the electrowinning is carried out.
- 25 4. The method according to claim 3, wherein the measuring of the redox potential of the feed stream is carried out continuously and the redox agent is added to maintain the measured value substantially equal to the optimum value.
- 30 5. The method according to claim 3 or 4, wherein the optimum value falls within a predetermined range and the measured value is maintained at a value within the predetermined range.

6. The method according to any one of the preceding claims, wherein the redox agent is added by mixing the redox agent with the electrolyte prior to the addition of the electrolyte to the electrolysis cell.
5
7. The method according to claim 6, wherein the redox agent is added to cold spent electrolyte which is recycled from the electrolysis cell.
10
8. The method according to claim 3, wherein the feed stream comprises spent electrolyte from the electrolysis cell.
15
9. The method according to claim 3, wherein the feed stream comprises overflow electrolyte from the electrolysis cell.
20
10. The method according to claim 3, wherein the measuring of the redox potential of the feed stream is carried out using a pair of electrodes located in the feed stream.
25
11. The method according to claim 10, wherein the pair of electrodes comprises a working electrode and a reference electrode.
30
12. The method according to claim 11, wherein the working electrode comprises a graphite electrode.
35
13. The method according to claim 11, wherein the working electrode comprises a platinum electrode.
14. The method according to claim 1, wherein the redox agent comprises a peroxide.

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15. The method according to claim 14, wherein the peroxide is hydrogen peroxide.
- 5 16. The method according to claim 1, wherein the redox agent is added in a continuous fashion.
17. The method according to claim 1, wherein the redox agent is added in a batchwise fashion.
- 10 18. A method of removing MnO₂ precipitate in a process for the electrowinning of a metal from an electrolyte, which comprises the steps of: measuring the redox potential of the electrolyte to obtain a measured value;
- 15 comparing said measured value with a predetermined optimum value; and adding a redox agent to the electrolyte to adjust the redox potential of the electrolyte to said optimum value.
- 20 19. The method according to claim 18, wherein the metal is zinc and the redox agent is hydrogen peroxide.
- 25 20. The method according to claim 18, wherein the redox agent comprises a peroxide.
21. The method according to claim 20, wherein the peroxide is hydrogen peroxide.
- 30 22. The method according to claim 18, wherein the redox agent is added in a continuous fashion.
23. The method according to claim 18, wherein the redox agent is added in a batchwise fashion.

24. In a zinc electrowinning process, a method of reducing MnO₂ formation in an electrolysis cell, comprising the steps of:
 - 5 measuring the redox potential of the electrolyte to obtain a measured value;
 - comparing the measured value with a predetermined optimum value; and
 - 10 adding a redox agent to the electrolyte to adjust the redox potential of the electrolyte to the optimum value.
25. The method according to claim 24, wherein the redox agent comprises a peroxide.
- 15 26. The method according to claim 25, wherein the peroxide is hydrogen peroxide.
- 20 27. In a zinc electrowinning process, a method of reducing current efficiency loss in an electrolysis cell, comprising the steps of:
 - measuring the redox potential of the electrolyte to obtain a measured value;
 - comparing the measured value with a predetermined optimum value; and
 - 25 adding a redox agent to the electrolyte to adjust the redox potential of the electrolyte to the optimum value.
- 30 28. The method according to claim 27, wherein the redox agent comprises a peroxide.
29. The method according to claim 28, wherein the peroxide is hydrogen peroxide.

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30. The method according to claim 24 or claim 27, wherein the cell comprises an anode pickling or aging cell.
- 5 31. In a zinc electrowinning process, a method of continuous on-line cell cleaning of MnO₂, comprising the steps of:
measuring the redox potential of the electrolyte to obtain a measured value;
10 comparing the measured value with a predetermined optimum value; and
adding a redox agent to the electrolyte to adjust the redox potential of the electrolyte to the optimum value.
- 15 32. In a zinc electrowinning process, a method of semi-continuous on-line cell cleaning of MnO₂, comprising the steps of:
measuring the redox potential of the electrolyte to obtain a measured value;
20 comparing the measured value with a predetermined optimum value; and
adding a redox agent to the electrolyte to adjust the redox potential of the electrolyte to the optimum value.
- 25 33. Apparatus for controlling the redox potential of an electrolyte, comprising:
a redox potential measuring device for measuring the redox potential of an electrolyte to produce an output measurement value; and
30 a redox controller responsive to the output measurement value for controlling the addition of redox agent to the electrolyte of an electrolysis cell.
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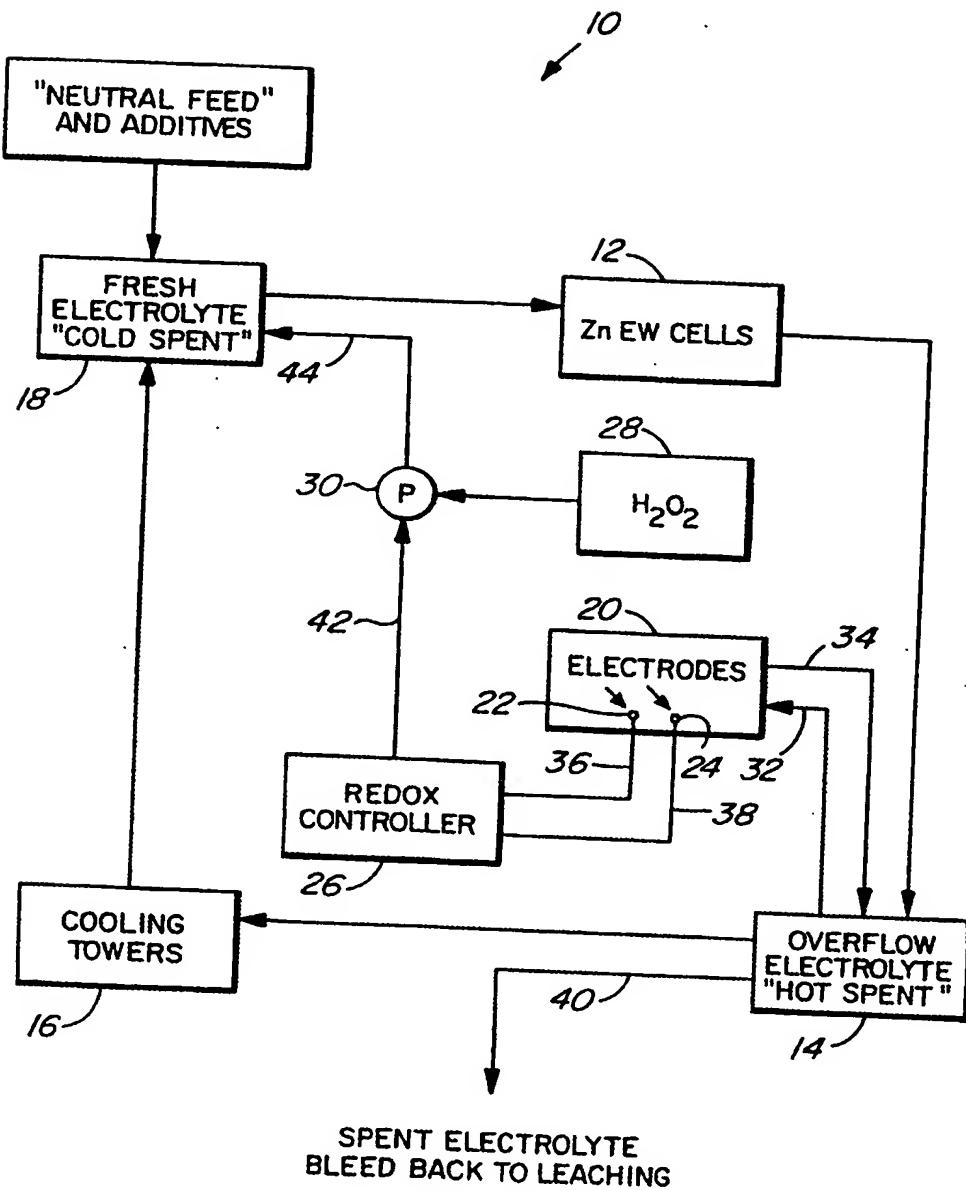
34. The apparatus according to claim 33, wherein the redox potential measuring device comprises a housing for the flow of electrolyte therethrough and a pair of electrodes for measuring the redox potential of an electrolyte flowing through the housing.
5
35. The apparatus according to claim 34, wherein the pair of electrolytes comprises a working electrode and a reference electrode.
10
36. The apparatus according to claim 35, wherein the working electrode comprises a graphite electrode.
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37. The apparatus according to claim 35, wherein the working electrode comprises a platinum electrode.
15
38. The apparatus according to claim 33, wherein the redox potential measuring device comprises a colorimeter for providing an indirect measurement of the redox potential.
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SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/CA 96/00366

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C25C7/06 C25C1/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C25C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 616 159 (OUTOKUMPU OY) 9 December 1988 see page 9; claims 1-8 ---	1
X	US,A,4 211 630 (C.C. BLAKE) 8 July 1980 see column 6 - column 8; claims 1-4 ---	33
A	US,A,4 071 421 (I. M. MASTERS) 31 January 1978 see column 3, line 15 - line 38 ---	1
A	US,A,5 180 563 (WEN-CHAO LAI) 19 January 1993 see column 6, line 15 - line 20 -----	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search 14 August 1996	Date of mailing of the international search report 02. 09. 96
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Groseiller, P

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No
PCT/CA 96/00366

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
FR-A-2616159	09-12-88	AU-B-	1690688	08-12-88
		DE-A-	3819020	15-12-88
		JP-A-	63312991	21-12-88
		NL-A-	8801406	02-01-89
US-A-4211630	08-07-80	GB-A-	1445505	11-08-76
		DE-A-	2528140	15-01-76
		FR-A,B	2276402	23-01-76
		JP-C-	1176934	14-11-83
		JP-A-	51018212	13-02-76
		JP-B-	58005994	02-02-83
		US-A-	4186067	29-01-80
US-A-4071421	31-01-78	CA-A-	1066656	20-11-79
		AU-B-	586037	13-12-79
		AU-B-	2773477	15-02-79
		BE-A-	857654	01-12-77
		DE-A-	2736232	16-02-78
		FR-A,B	2361482	10-03-78
		GB-A-	1525458	20-09-78
		JP-A-	53021035	27-02-78
		NL-A-	7708712	14-02-78
US-A-5180563	19-01-93	NONE		